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**Published**
*With international search report.*
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(54) Title: FLUORINATED ETHERS

(57) Abstract

A fluorinated ether which is the product of a fluorination reaction of an adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether. The fluorinated ethers are useful as inert fluids, especially as the working fluid of a heat pump.

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 84/00013 (SA 6462)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/05/84

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| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|---|---|---|---|---|
| US-A- 3816286 | 11/06/74 | GB-A- | 1430583 | 31/03/76 |
| US-A- 2644823 | | None | | |

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82

International Application No. PCT/GB 84/00013

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. [X] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND NOT COMPLETELY SEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. [ ] Claim numbers .......... because they relate to subject matter 13 not required to be searched by this Authority, namely:

2. [ ] Claim numbers .......... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out 13, specifically:

3. Claim numbers searched incompletely: 1-9, 11, 12.

In the light of the general wording of claims 1-9,11,12 the search has been carried out with reference to the examples.

VI. [X] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 11

This International Searching Authority found multiple inventions in this international application as follows:

- 1-12 : Fluorinated ethers and process for their preparation
- 13-15 : Use of fluorinated ethers as working fluids and coolants, and heat pump containing fluorinated ethers
- 16 : Use of fluorinated ethers as fluid for vapour phase soldering
- 17 : Use of fluorinated thers as lubricants

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. [X] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers: 1-12.

4. [ ] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

[ ] The additional search fees were accompanied by applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

aryl, provided that both groups are not aryl. The preferred alkyl groups are methyl, ethyl and propyl but may also be butyl or larger groups.

Among the preferred hydrogen-containing ethers which may be used in accordance with the present invention are dimethyl ether, diethyl ether, dipropyl ether, tetrahydrofuran, dioxane, tetrahydropyran, trimethylene oxide, or ethylene glycol dimethyl ether.

The preferred fluoro-olefin is tetrafluoro-ethylene. Other fluoro-olefins which may be used are difluoroethylene, chlorotrifluoroethylene, perfluorcyclobutene, trifluroethylene and hexafluoropropene. The mole ratio of the fluoro-olefin and the hydrogen-containing ether in the adduct may be from 6:1 to 1:1, but in certain instances may involve a larger amount of fluoro-olefin. For many working fluid applications, particularly for heat pump applications, it is preferred that the ratio of fluoro-olefin to the hydrogen-containing ether in the adduct is 2:1 or 1:1. The fluorinated ether according to the present invention may be one of the following compounds:

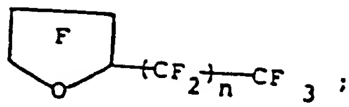
# FLUORINATED ETHERS

This invention relates to certain fluorinated ethers and to the use of the fluorinated ethers in a number of diverse fields, especially as inert fluids, for example the working fluid of a heat pump.

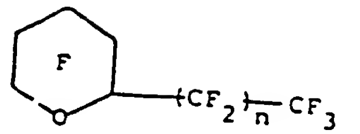
The invention relates to novel fluorinated ethers which are the product of a fluorination reaction of an adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether. The fluorinated ether may be partially or fully fluorinated during the fluorination reaction. The hydrogen-containing ether is preferably of the formula R-O-R' wherein R and R' are hydrocarbon groups optionally substituted by chlorine or fluorine or together form a single hydrocarbon group and the total number of carbon atoms in the groups R and R' is preferably less than 10; specifically groups R and R' may be the same or different and maybe selected from alkyl, cycloalkyl, aralkyl and

The present invention also includes a process for making fluorinated ethers as described above wherein the fluorination of the adduct is effected by the use of a high valency metal fluoride as a fluorinating agent at a temperature above 200°C. A fluorination procedure of this general kind is described in "Advances in Fluorine Chemistry" Vol 1. Butterworth, 1960 P 166. Cobalt trifluoride alone or in association with alkali or alkaline earth metal fluorides such as potassium fluoride or calcium fluoride are the preferred fluorinating agents. In the process of this invention, the fluorination is preferably effected in the temperature range 300°C to 600°C eg. at temperatures between 400°C to 500°C.

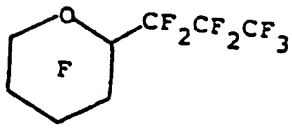
The present invention is concerned with compounds which have good stability and by suitable selection compounds are provided for use as inert fluids and in particular for the working fluid of a heat pump. Furthermore, compounds may be selected which are particularly useful as heat pipe fluids, as coolants, as heat absorption media eg. for geothermal heat recovery, as lubricants, in vapour phase soldering, as solvents, especially in the separation of ethyl alcohol from aqueous mixtures, or as dielectrics. Several of these



n = 1, 2, 3



n = 1, 2, 3



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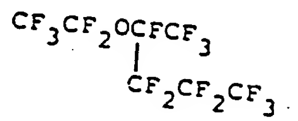

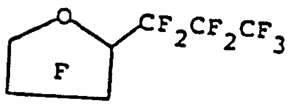

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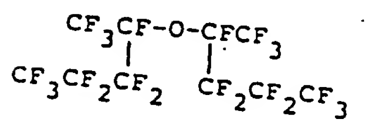

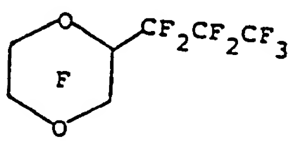

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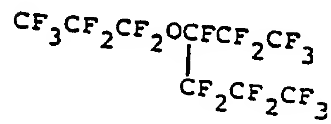
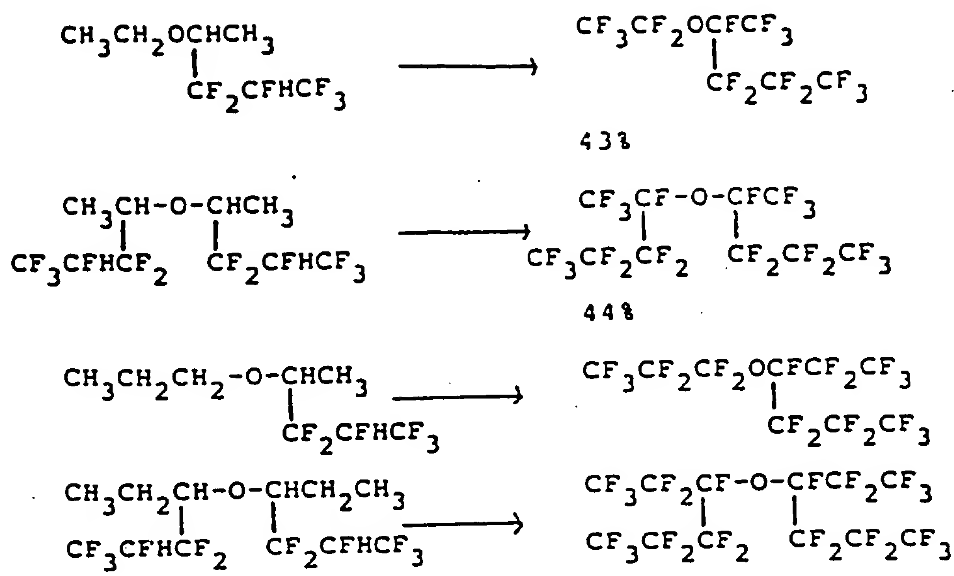


In the above formulae the symbol F in the centre of the rings depicted indicates that all unmarked bonds are to fluorine atoms. This designation is used thoughout the specification.

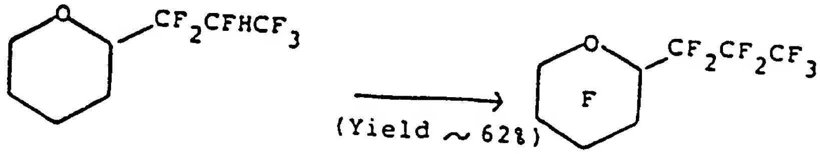
Fluorination with cobalt trifluoride is a technique well known in the art and is described in standard text books, for example R.D. Chambers "Fluorine in Organic Chemistry", see page 25. As is known, cobalt trifluoride can be re-generated by reacting elemental fluorine and the cobalt difluoride resulting from the organic fluorination reaction.

There is set out below a number of fluorination reactions in accordance with the present invention which have been carried out. All these fluorination reactions were effected, as indicated using cobalt trifluoride at 440°C.

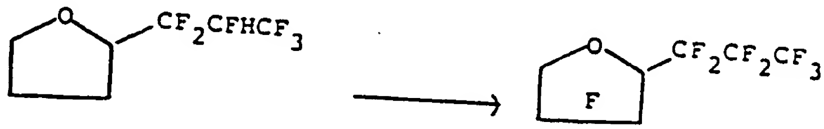
uses require the fluorinated ether to have particularly high stability, which is a feature of the compounds of this invention. Furthermore, the use of partly fluorinated compounds as starting materials for the fluorination reaction in some cases substantially avoids, and not merely inhibits fragmentation of the adducts: additionally the fluorine containing adducts used in accordance with this invention permit controlled yields to be obtained with respect to various fluorinated ethers. It is known (see Journal of Fluorine Chemistry 1975 5 p 521 - Brandwood, Coe, Ely and Tatlow) that the usual experience with fluorination of hydrocarbon material containing no fluorine is the production of a complicated mixture of fluorinated and partially fluorinated products, including the products of fragmentation. In using the process of this invention employing cobalt trifluoride as a fluorinating agent at elevated temperatures complete fluorination can be effected if the temperature employed is of the order of 440°C, for the adducts exemplified in this specification. The selection of lower temperatures, but above 200°C, results in the production of partially fluorinated ethers.



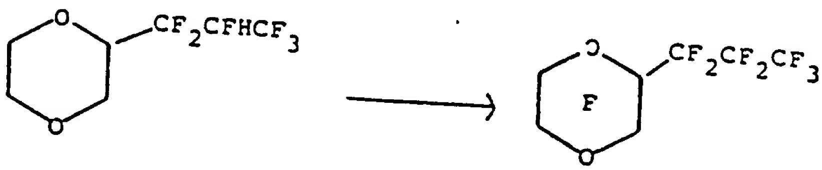

The use of the above-described cobalt trifluoride technique the fluorination of an adduct in accordance with the present invention enables the temperature dependance of the fluorination technique using cobalt trifluoride to be determined. The following Table I gives the results of experiments conducted at various temperatures using cobalt trifluoride and the adduct 2-(2-hydrohexafluoropropyl)oxolane. At temperature below about 200°C virtually no fully fluorinated ether is produced. On the other hand, at a temperature of 440°C very little product results other than an excellent yield of the fully fluorinated adduct.



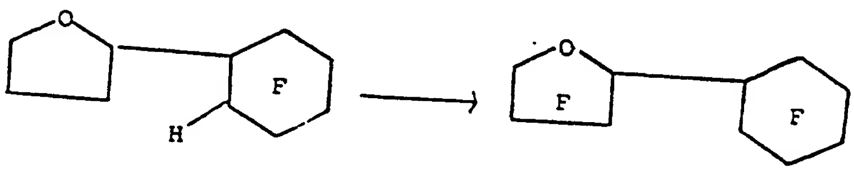

(Yield ~ 62%)



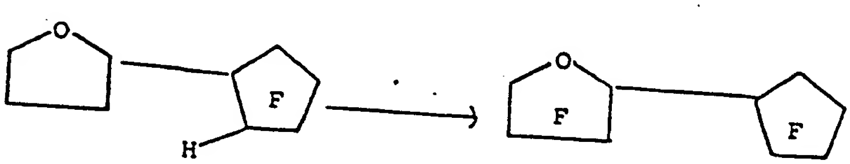

(Yield ~70%)



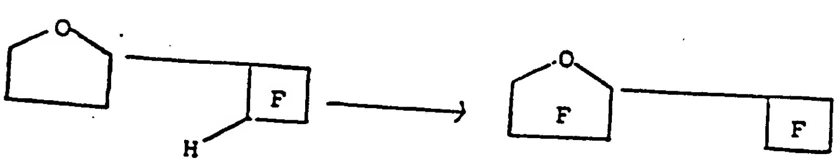

(Yield ~ 67%)




(Yield 60%)




(Yield 65%)



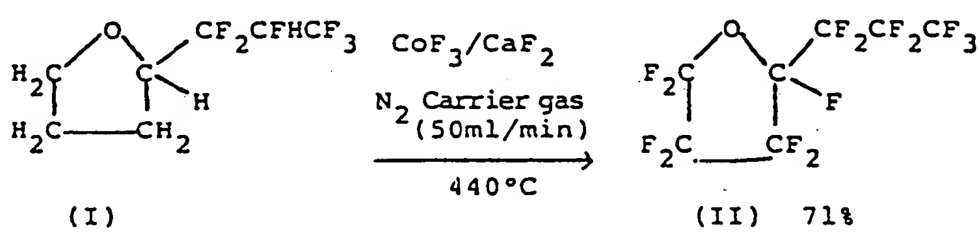

(Yield 64%)

The following Examples illustrate in detail the preparation of fluorinated ethers in accordance with the present invention

Example 1

Preparation of Perfluoro-2-Propyloxolane

2-(1,1,2,3,3,3,-hexafluoropropyl) oxolane was fluorinated with cobalt trifluoride/$CaF_2$ to produce perfluoro-2-propyloxolane (II) in good yield.

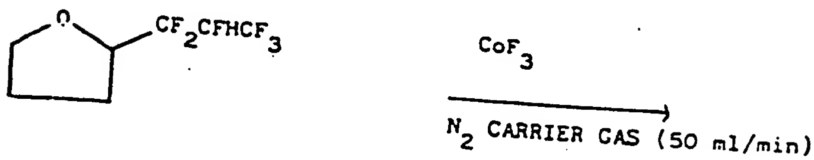


Experimental procedure

The fluorinating reagent (approx 330g) was generated by passing fluorine gas through a bed composed of 150g of cobalt difluoride and 150g of calcium difluoride until fluorine was detected at the bed outlet using

TABLE I

Temperature Dependance of the Cobalt Trifluoride Fluorination of 2-(2-hydrohexafluoropropyl) oxolane




| % Yield | Temperature(°C) | $\%C_7F_{14}O$ | $\%C_7F_{13}HO$ | $\%C_7F_{12}H_2O$ | $\%C_7F_{11}H_3O$ | $\%C_7F_{10}H_4O$ and less-fluorinated derivatives |
|---|---|---|---|---|---|---|
| 30%[a] | 110 | trace | 1.3 | 3.7 | 23.3 | 71.1 |
| 49%[b] | 160 | trace | 1.5 | 7.5 | 69.8 | 21.3 |
| 79%[b] | 240 | 0.4 | 1.2 | 14.8 | 63.7 | 19.7 |
| 70%[c] | 270 | 2.8 | 20.9 | 29.2 | 42.9 | 2.4 |
| 73%[d] | 355 | 13.6 | 46.3 | 14.2 | 7.8 | - |
| ~ 70%[e] | 440 | ~ 95% | ~1% | - | - | - |

a) Based on $C_7F_6H_8O \longrightarrow C_7F_{10}H_4O$

b) Based on $C_7F_6H_8O \longrightarrow C_7F_{11}H_3O$

c) Based on $C_7F_6H_8O \longrightarrow C_7F_{12}H_2O$

d) Based on $C_7F_6H_8O \longrightarrow C_7F_{13}HO$

e) Based on $C_7F_6H_8O \longrightarrow C_7F_{14}O$

Pure samples of the component fluorinated ethers of the reaction mixture can be isolated by conventional techniques. It is possible to "tailor" a particular fluorinated ether for a particular use. However, it is also possible to prepare mixtures of materials, appropriate to specific uses, by one of the three following methods:

(a) Mixing pure components,
(b) Partial fluorination of a single adduct,
(c) Fluorination of mixed adducts.

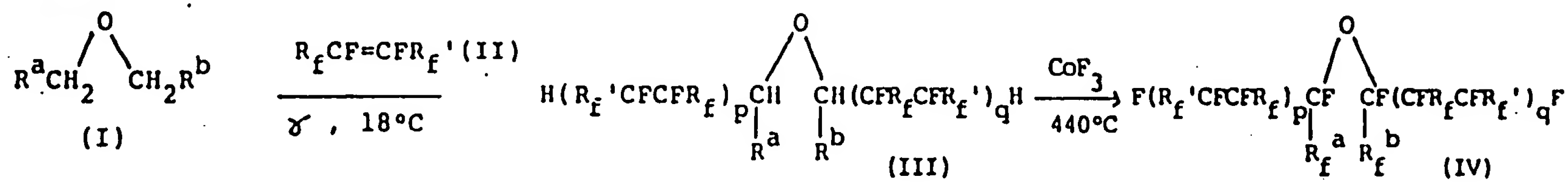
starch/iodide paper. Nitrogen gas was passed through the bed at 50ml/min for 30 minutes at the required temperature of 440°C. The oxolane compound I (1.93g, 8.7mmol) was added dropwise at a rate of about 1 ml in 10 minutes, and the products collected in a trap cooled by liquid air. The bed was flushed out with nitrogen for 15 minutes. The trap was warmed up to room temperature, anhydrous sodium carbonate was added to remove dissolved hydrogen fluoride, and the colourless liquid (2.27 g) separated. The liquid was distilled at atmospheric pressure to give perfluoro-2-propyl-oxolane, Bpt 79°C, with a yield of 71%.

Example 2

The addition of a variety of ethers (I) to the fluoroalkenes (II) was carried out using $\gamma$-ray initiation of the reaction at ambient temperature to give the adduct (III), or a mixture of such adducts. The adduct(s) (III) were separated, purified and individually fluorinated using a cobalt trifluoride catalyst at a temperature of 440°C to give a variety of perfluoroethers (IV) and by-products (V). The results are summarised in Table II :

# TABLE II

## ADDITION OF ETHERS TO PERFLUOROALKENES AND FLUORINATION TO PRODUCE PERFLUOROETHERS




where $R_f^a$ and $R_f^a$ represent the groups $R^a$ and $R^b$ respectively with all the hydrogen atoms replaced by fluorine.

+ BY-PRODUCTS (V)

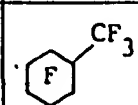
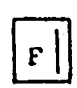
| STARTING ETHER (I) | PERFLUORO-ALKENE (II) | ADDUCT (III) | % YIELD (III) | PERFLUORO-ETHER (IV) | % YIELD (IV) | Bpt (IV) | BY PRODUCTS (V) | % YIELD (V | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_2O$ | $CF_2{=}CFCF_3$ | p=1,q=0 | 68 | p=1, q=0 | 36 | - | $CF_3(CF_2)_2CF_3$ | 44 | 1 |
| |  | p=1, q=0 | 78 | p=1, q=0 | 16 | |  | 9 | 2 |
| |  | p=1, q=0 | 74 | Complex mixture of Products | | | | | 3 |

TABLE II (Continued)

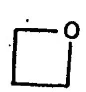
| STARTING ETHER (I) | PERFLUORO-ALKENE (II) | ADDUCT (III) | % YIELD (III) | PERFLUORO-ETHER (IV) | % YIELD (IV) | Bpt (IV) | BY PRODUCTS (V) | % YIELD (V) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|---|---|---|
| $(CH_3CH_2)_2O$ | $CF_2=CFCF_3$ | p=1, q=0 | 38 | p=1, q=0 | 43 | 78 | $CF_3(CF_2)_3CF_3$ | 10 | 4 |
| | | p=1, q=1 | 43 | p=1, q=1 | 41 | 136 | $CF_3(CF_2)_3CF_3$ | 9 | 5 |
| $(CH_3CH_2CH_2)_2O$ | $CF_2=CFCF_3$ | p=1, q=0 | 12 | p=1, q=0 | 32 | 137 | - | - | 6 |
| | | p=1, q=1 | 28 | p=1, q=1 | 12 | 162 | $CF_3(CF_2)_4CF_3$ | 30 | 7 |
| $(CH_3CH_2CH_2CH_2)_2O$ | $CF_2=CFCF_3$ | p=1, q=0 | 16 | p=1, q=0 | 18 | 149 | $CF_3(CF_2)_5CF_3$ | 10 | 8 |
| | | p=1, q=1 | 28 | - | - | - | $CF_3(CF_2)_5CF3$ | 32 | 9 |
| $(CH_3OCH_2)_2$ | $CF_2=CFCF_3$ | $CH_3OCHCH_2OCH_3$ <br> $\mid$ <br> $CF_2CFHCF_3$ | 53 | Complex mixture of Products | | | | | 10 |
|  | $CF_2=CFCF_3$ | p=1, q=0 | 65 | p=1, q=0 | 8 | - | $CF_3(CF_2)_4CF_3$ <br> $CF_3(CF_2)_3CF_3$ | 10 <br> 3 | 11 |

TABLE II (Continued)

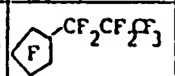
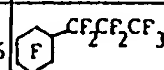
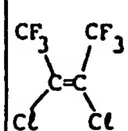
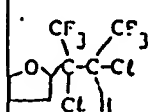
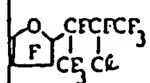
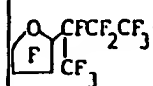
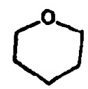
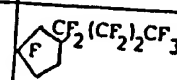
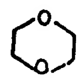
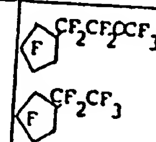
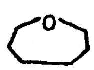
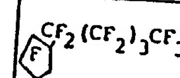
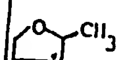
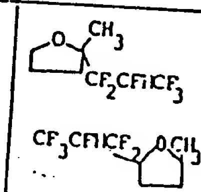
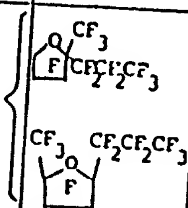
| STARTING ETHER (I) | PERFLUORO-ALKENE (II) | ADDUCT (III) | % YIELD (III) | PERFLUORO-ETHER (IV) | % YIELD (IV) | Bpt (IV) | BY PRODUCTS (V) | % YIELD (V) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|---|---|---|
|  | $CF_2=CFCF_3$ | p=1, q=0 | 95 | p=1, q=0 | 70 | 79 | $CF_3(CF_2)_4CF_3$ | 5 | 12 |
| | $CF_3CF=CFCF_3$ | p=1, q=0 | 89 | p=1, q=0 | 53 | 101 | - | - | 13 |
| | $CF_2=CFCl$ | p=1, q=0, $R_f' = Cl$ | 78 | p=1, q=0, $R_f' = Cl$<br>p=1, q=0, $R_f' = F$ | 45<br>12 | 82<br>54 | - | - | 14 |
| |  | p=1, q=0 | 91 | p=1, q=0 | 64 | - | - | - | 15 |
| |  | p=1, q=0 | 83 | p=1, q=0 | 65 | 117 |  | 11 | 16 |
| |  | p=1, q=0 | 91 | p=1, q=0 | 51 | 136 |  | 6 | 17 |
| |  |  | 89 | <br> | 16<br>15 | -<br>101 | -<br>- | -<br>- | 18 |

TABLE II (Continued)

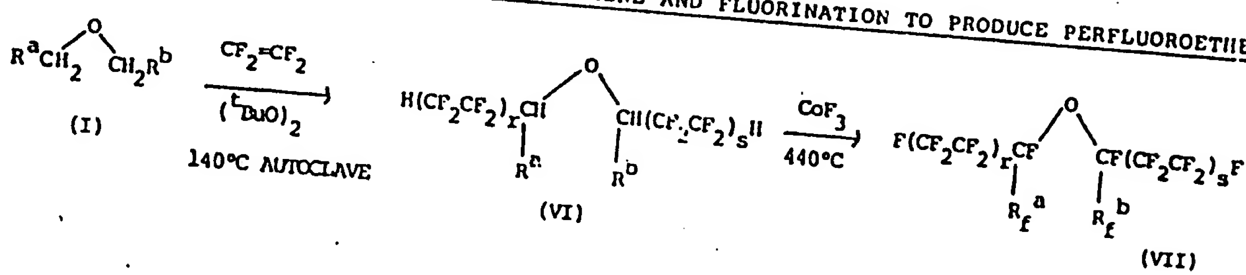
| STARTING ETHER (I) | PERFLUORO-ALKENE (II) | ADDUCT (III) | % YIELD (III) | PERFLUORO-ETHER (IV) | % YIELD (IV) | Bpt (IV) | BY PRODUCTS (V) | % YIELD (V) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|---|---|---|
|  | $CF_2{=}CFCF_3$ | p=1, q=0 | 61 | p=1, q=0 | 62 | - | - | - | 19 |
| |  | p=1, q=0 | 76 | p=1, q=0 | 31 | 134 |  | 20 | 20 |
|  | $CF_2{=}CFCF_3$ | p=1, q=0 | 79 | p=1, q=0 | 68 | 90 | - | - | 21 |
| |  | p=1, q=0 | 49 | p=1, q=0 | 17 | 125 |  | 8<br>10 | 22 |
|  | $CF_2{=}CFCF_3$ | p=1, q=0 | 70 | p=1, q=0 | 45 | 124 | $CF_3(CF_2)_6CF_3$ | 12 | 23 |
| |  | p=1, q=0 | 71 | p=1, q=0 | 20 | 158 |  | 22 | 24 |
|  | $CF_2{=}CFCF_3$ |  | 96 |  | 18<br>25 | 101<br>94 | $CF_3CF_2CF(CF_3)(CF_2)_2CF_3$ | 10 | 25 |

Example 3

The addition of a variety of ethers (I) to tetrafluoroethene ($CF_2=CF_2$) was carried out using a tertiary butyl peroxide catalyst at a temperature of 140°C in an autoclave. Each ether (I) gave a mixture of adducts (VI) which were separated and fluorinated individually using a cobalt trifluoride catalyst at a temperature of 440°C to give the perfluoroethers (VII). The results are summarised in Table III:

## TABLE III

### ADDITION OF ETHERS TO TETRAFLUOROETHENE AND FLUORINATION TO PRODUCE PERFLUOROETHERS



where $R_f^a$ and $R_f^b$ represent the groups $R^a$ and $R^b$ respectively with all the hydrogen atoms replaced by fluorine.

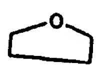
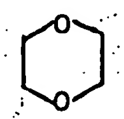
| STARTING ETHER (I) | ADDUCT (VI) | % YIELD (VI) | PERFLUOROETHER (VII) | % YIELD (VII) | Bpt (°C) (VII) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|
|  | r=1, s=0 | 61 | r=1, s=0 | 65 | 54 | 1 |
| | r + s = 2 | 30 | r=1, s=1<br>r=2, s=0 | 65-70 | 93<br>- | 2 |
| | r + s = 3 | 8 | r=2, s=1<br>r=3, s=0 | 61 | 132<br>141 | 3 |
| | r = s = 4 | 0.8 | r=3, s=1<br>r=4, s=0 | 55 | -<br>- | 4 |

TABLE III (Continued)

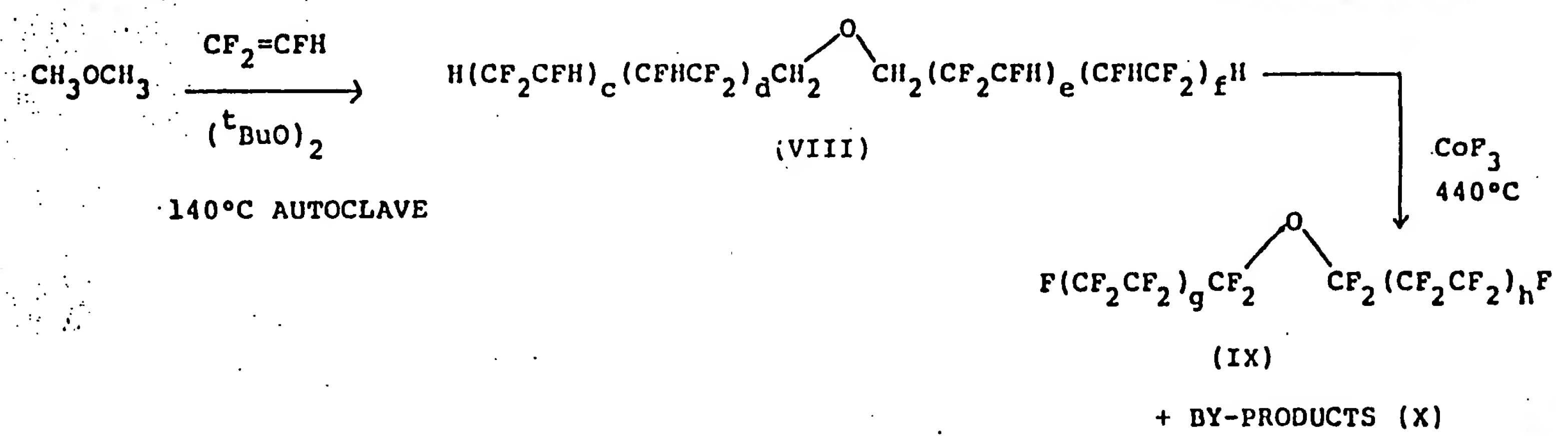
| STARTING ETHER (I) | ADDUCT (VI) | % YIELD (VI) | PERFLUOROETHER (VII) | % YIELD (VII) | Bpt (°C) (VII) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|
|  | r=1, s=0 | 57 | r=1, s=0 | 33 | 65 | 5 |
| | r + s = 2 | 30 | r=1, s=1<br>r=2, s=0 | 34 | 103<br>110 | 6 |
| | r + s = 3 | 11 | r=2, s=1<br>r=3, s=0 | 38 | 141<br>150 | 7 |
| | r + s = 4 | 2 | r=3, s=1<br>r=4, s=0 | 35 | 174<br>180 | 8 |
| $(CH_3CH_2)_2O$ | r=1, s=0 | 51 | r=1, s=0 | 23 | 56 | 9 |
| | r + s = 2 | 37 | r + s = 2 | 31 | 98 | 10 |
| | r + s = 3 | 10 | r + s = 3 | 35 | - | 11 |
| | r + s = 4 | 2 | r + s = 4 | 35 | - | 12 |

Example 4

Dimethyl ether was added to trifluoroethene by a free-radical reaction using a tertiary butyl peroxide catalyst at a temperature of 140°C in an autoclave. The product mixture was separated into the adduct isomer mixtures (VIII) which were fluorinated using a cobalt trifluoride catalyst at a temperature of 440°C to give the perfluoroethers (IX) the by-products (X). The results are summarised in Table (IV):

TABLE IV

ADDITION OF DIMETHYLETHER TO TRIFLUOROETHENE AND FLUORINATION TO PRODUCE PERFLUOROETHERS




| ADDUCT (VIII) | % YIELD (VIII) | PERFLUOROETHER (IX) | % YIELD (IX) | Bpt (IX) (°C) | BY-PRODUCTS (X) | % YIELD (X) | EXPERIMENT NUMBER |
|---|---|---|---|---|---|---|---|
| c+d+e+f = 1 | 62 | UNIDENTIFIED MIXTURE OF PERFLUORINATED PRODUCTS | | | | | 1 |
| c+d+e+f = 2 | 30 | g = 2, h = 0 | 14 | 62 | - | - | 2 |
| c=d=e=f = 3 | 6 | g = 3, h = 0<br>g = 2, h = 1 | 7<br>3 | 106<br>- | $CF_3(CF_2)_4CF_3$<br>$CF_3(CF_2)_5CF_3$ | 29<br>12 | 3 |

It is to be understood that in making the novel fluorinated ethers according to the present invention other techniques for fluorinating the adducts may be employed, for example elemental fluorine or $ClF_3$ or electrochemical fluorination may be employed.

In many working fluid situations the working fluid is exposed to cyclic temperature changes, and the fluorinated ethers according to this invention provide compounds or mixes of compounds which are suitable for this purpose. The fluorinated ethers may be employed in an apparatus in which there is transfer of heat from a higher to a lower temperature, or alternatively in an apparatus where there is transfer of heat from a lower to a higher temperature. Furthermore, it is to be noted that the fluorinated ethers may be used in apparatus in which there is a change from a liquid to a vapour state, and back to the liquid state, such as is the case with the heat pump. A particular use where a change of state is involved is in using these working fluids in a refrigerator: another use is in the transfer of heat in chemical reactors and the like. One particular situation where the fluorinated ethers of this invention may be used with advantage is in the generation of power, for

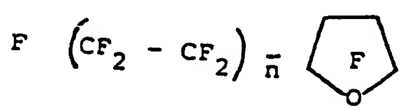
example Organic Rankine Cycle power generation or the abstraction of heat from geothermal sources, including the conversion of geothermal energy to work.

The compounds or mixtures of compounds according to the invention for use as the working fluid in a heat pump may be chosen so as to provide the desired critical temperature and boiling point. Other factors are relevant, but these are the prime ones. The critical temperature and boiling point desired will depend upon the condensing and evaporating temperatures used in the heat pump.

A suitable substance for use as a working fluid in a heat pump condensing at $T_C$ and evaporating at $T_E$ would have a critical temperature substantially higher than $T_C$ and a normal boiling point substantilly lower than $T_E$. Thus for example, if $T_C = 150°C$ and $T_E = 100°C$, a possible working fluid would be 1.1.1.2.3.3. hexafluoro butyl methyl ether which has a critical temperature of 236°C and a normal boiling point of 87°C, or perfluoro-2-propyloxolane which has a critical temperature of 206°C and a normal boiling point of 79°C.

Adducts formed by reacting tetrafluoroethylene

$(CF_2 = CF_2)$ with hydrogen containing, eg. hydrocarbon, ethers are formed as mixtures of products. The reaction tends to produce telomers of the type $H\ (CF_2 - CF_2)_n$ - R O R' where n may be from 1 to well above 8. Fluorination of these telomer mixtures can produce mixtures of compounds according to the invention having boiling points, critical temperatures and other properties suiting them for particular uses. For instance, when tetrafluoroethylene is reacted to add to tetrahydrofuran the products after fluorination have the formula:




Products are obtained which are useful, for example, as follows:

| | | |
|---|---|---|
| for low values of n | - | working fluids and coolants, |
| intermediate values of n | - | fluids for vapour phase soldering, and |
| higher values of n | - | lubricants |

CLAIMS:

1. A fluorinated ether which is the product of a fluorination reaction of an adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether.

2. An ether as claimed in claim 1 which is fully fluorinated during the said fluorination reaction.

3. An ether as claimed in claim 1 or claim 2 wherein the hydrogen-containing ether is of the formula R-O-R' wherein R and R' are hydrocarbon groups or together form a single hydrocarbon group and the total number of carbon atoms in the hydrocarbon groups R and R' is up to 10.

4. An ether is claimed in claim 3 wherein the groups R and R' are the same or different and are methyl, ethyl, propyl or butyl groups.

5. An ether as claimed in claim 3 wherein the groups R and R' contain halogen.

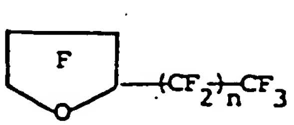
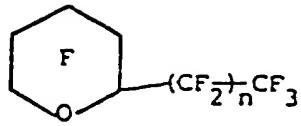
6. An ether as claimed in any one of the preceding claims wherein the fluoro-olefin is tetrafluoro-ethylene or hexafluoropropene.

7. An ether is claimed in any one of the preceding claims wherein the hydrogen-containing ether used in forming the adduct is dimethyl ether, diethyl ether, dipropyl ether, tetrahydrofuran, dioxane, tetrahydropyran, trimethylene oxide, or ethylene glycol dimethyl ether.

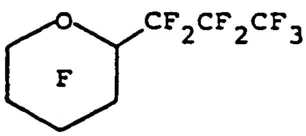
8. An ether as claimed in any one of the preceding claims wherein the ratio of the fluoro-olefin to the hydrogen-containing ether in the adduct is 6:1 to 1:1.

9. An ether as claimed in any one of the preceding claims wherein the ratio of the fluoro-olefin to the hydrogen-containing ether in the adduct is 2:1 or 1:1.

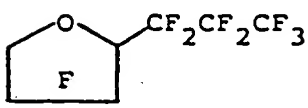
10. An ether as claimed in claim 1 which is the product of a fluorination reaction and is one of the following :

 ;  ;

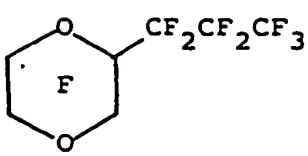
n = 1, 2, 3 n = 1, 2, 3

 ;

$CF_3CF_2OCFCF_3$
$\quad\quad\quad\;\; |$
$\quad\quad\quad\; CF_2CF_2CF_3$ ;

 ;

$CF_3CF\text{-}O\text{-}CFCF_3$ ;
$\quad\quad\;\; | \quad\quad\;\; |$
$CF_3CF_2CF_2 \quad CF_2CF_2CF_3$ ;

 ; or

$CF_3CF_2CF_2OCFCF_2CF_3$
$\quad\quad\quad\quad\quad\;\; |$
$\quad\quad\quad\quad\quad CF_2CF_2CF_3$

11. A process for the preparation of an ether as claimed in any one of the preceding claims wherein the fluorination of the adduct formed by the free-radical addition of a fluoro-olefin and a hydrogen-containing ether is effected by the use of cobalt trifluoride as a fluorinating agent at a temperature of above 200°C.

12. A process is claimed in claim 11 wherein the temperature employed is in the range of from 400°C to 450°C.

13. The use as a working fluid of a fluorinated ether as claimed in any one of the claims 1 to 10.

14. A heat pump wherein the working fluid employed is a fluorinated ether as claimed in any one of claims 1 to 10.

15. The use as a coolant of a compound as claimed in claim 1 and of the formula R' O R - $(CF_2 - CF_2)_n$ F wherein R' O R- is the fluorinated residue of a hydrogen containing ether and n is from 2 to 4.

16. The use as a fluid for vapour phase soldering of a compound as claimed in claim 1 and of the formula R' O R- $(CF_2 - CF_2)_n$ F wherein R' O R- is the fluorinated residue of a hydrogen containing ether and n is from 4 to 7.

17. The use as a lubricant of a compound as claimed in claim 1 and of the formula R' O R- $(CF_2 - CF_2)_n$ F wherein R' O R- is the fluorinated residue of a hydrogen containing ether and n is 8 or more.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 84/00013

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

$IPC^3$: C 07 D 307/18; 309/08; 319/12; C 07 C 43/12; 41/22; F 25 B 29/00; B 23 K 28/00; C 10 M 3/00

**II. FIELDS SEARCHED**

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| $IPC^3$ | C 07 D 307/00; C 07 D 309/00; C 07 D 319/00; C 07 C 43/00; C 07 C 41/00 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT** [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| X<br>Y | Chemical Abstracts, vol. 94, no. 5, 2 February 1981 (Columbus, Ohio, US) R.D. Chambers et al.: "Free radical chemistry. Part 2. Additions of dimethyl ether to F-cycloalkenes", see page 490, abstract no. 29806u, J. Fluorine Chem. 1980, 16(4), 351-64 (Eng.)<br>-- | 1,3,4,7-9, 11,12<br>6,7 |
| Y | US, A, 3816286 (R.N. HASZELDINE) 11 June 1974 see examples V, VI, XXVII<br>-- | 6,7 |
| X | US, A, 2644823 (E.A. KAUCK) 7 July 1953 see the entire document<br>------ | 10 |

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

**IV. CERTIFICATION**

| Date of the Actual Completion of the International Search [2] | Date of Mailing of this International Search Report [2] |
|---|---|
| 12th April 1984 | 29 JUIN 1984 |
| **International Searching Authority [1]** | **Signature of Authorized Officer [10]** |
| EUROPEAN PATENT OFFICE | G.L.M. Kruydenberg |

Form PCT/ISA/210 (second sheet) (October 1981)